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Diode laser absorption spectrometry for $^{13}CO_2/\,^{12}CO_2$ isotope ratio analysis: Investigation on precision and accuracy levels

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ABSTRACT Near-infrared laser spectroscopy is used to measure the $^{13}C/^{12}C$ isotope abundance ratio in gas phase carbon dioxide. The spectrometer, developed expressly for field applications, is based on a 2 μm distributed feedback diode laser in combination with sensitive wavelength modulation detection. It is characterized by a simplified optical layout, in which a single detector and associated electronics are used to probe absorptions of a pair of $^{13}CO_2$ and $^{12}CO_2$ lines, simultaneously in a sample, as well as a reference gas. For a careful investigation of the achievable precision and accuracy levels, we carried out a variety of laboratory tests on CO_2 samples with different isotopic compositions, calibrated with respect to the international standard material by means of isotope ratio mass spectrometry. The $1-\sigma$ accuracy of the $^{13}CO_2/^{12}CO_2$ determinations, reported in the so-called δ notation, is about 0.5‰ (including both statistical and systematic errors), for δ-values in the range from −30‰ to +20‰. We show that the major source of systematic errors is a consequence of the non-linearity of the Lambert–Beer absorption law, and can be corrected for to a very high degree of accuracy.

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1 Introduction

In the last few years, the need of new instruments for accurate, and possibly in-situ, determinations of stable isotope abundance ratios in simple molecules have become manifest [1, 2]. As it is well known, the standard method to perform isotope analysis is isotope ratio mass spectrometry (IRMS). After 40 years of development, IRMS instrumentation is commercially available and provides impressive levels of accuracy and precision, for carbon isotopes, typically between 0.01 and 0.1‰ depending on the experimental configuration. In spite of this, IRMS still presents a number of serious drawbacks. The instrumentation is voluminous and heavy, and requires a dedicated technician for maintenance and reliable operation, excluding its (widespread) use in many in-situ applications. Moreover, molecules of different isotopic make-up (isotopologues) that appear in the same mass channel cannot always be distinguished. Essentially for these reasons, there is a growing interest in alternatives for IRMS.

Nowadays, isotope analysis represents an outstanding tool for quantitative studies of complex natural phenomena. A large variety of physical, chemical, and biological processes discriminate among different isotopologues. As a result of these fractionation effects, in nature stable isotope abundance ratios show small variations. In this context, the measurement of ^{13}C and ^{12}C isotope abundances in carbon dioxide can be an extremely useful tool in environmental sciences. The abundance ratio $^{13}C/^{12}C$ is typically expressed relative to a standard material, as the so-called delta-value, through the formula:

$$\delta^{13}C = \left(\frac{R^{13}_{\text{sample}}}{R^{13}_{\text{reference}}} - 1 \right) \tag{1}$$

where R^{13} represents the ratio between the $[^{13}C]$ and $[^{12}C]$ atomic number densities. The $\delta^{13}C$-value is usually reported in per mil (‰) and is generally referred to the international PDB-standard (Belemnite of the Pee Dee Formation in South Caroline, $[^{13}C]/[^{12}C] = 1.12372 \times 10^{-2}$).

Analysis of carbon isotopes finds application in several research fields, including ecology [3], atmospheric chemistry [4] and geochemistry [5]. Carbon dioxide is the most important greenhouse gas and its contribution to the global warming, as well as its complex mechanisms of distribution in the oceans and in the biosphere, can be studied in-depth using $\delta^{13}C$ measurements. Similarly, $\delta^{13}C$ analysis is of the utmost importance in geochemical investigations of volcanic gases. Indeed, in gas-geochemistry, isotopic parameters enable researchers to understand source-region changes, which are fundamental to monitor and forecast volcanic activity. Nowadays, geochemical monitoring of volcanoes requires periodic sampling of gases followed by laboratory IRMS analysis, yielding results long after the samples are taken. As a consequence, isotope data are inevitably temporally sparse. Instead, regular and frequent observations of relevant isotope ratios, including $^{13}CO_2/^{12}CO_2$, would enhance the capabilities of isotope-geochemistry to closely monitor changes in volcanic activities. Hence, in-situ and continuous monitoring of carbon isotopes in CO_2 can lead to significant advances in carbon cycle research [6] as well as in geochemical surveillance of a volcano [7].

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It is mainly for the perspective of field applicability that laser spectroscopy is attracting a growing interest [8]. Hitherto, a number of feasibility studies and experimental demonstrations of isotope ratio analysis of CO_2 have been reported, that exploit the high sensitivity of the infrared spectrum to isotopic substitution. Perhaps the earliest successful measurements were carried out using the technique of non-dispersive infrared detection (NDIR). For a brief description and an overview of $^{13}CO_2$ analyses by NDIR, we refer to [8]. Although NDIR instruments are robust, simple and relatively low-cost, the technique is inherently of low spectral resolution, resulting in potential problems with gas selectivity. The laser-based studies have involved a variety of $^{13}CO_2/^{12}CO_2$ line pairs mostly in the spectral region around 4.3 μm, using liquid-nitrogen cooled lead salt diode lasers [9, 10] or coherent sources based on difference frequency generation in a periodically poled $LiNbO_3$ crystal [11]. A few attempts have been made in the near-infrared, using telecommunications diode lasers [12, 13], which offer some relevant advantages, including room-temperature and reliable operation, as well as low cost and small size. Interesting results have been obtained by Crosson and co-workers, who compensated for the very weak line intensity at a wavelength of 1.6 μm (about 5 orders of magnitude lower than in the 4.3 μm region) using the ultra-sensitive, albeit more complicated, technique of cavity ring-down spectroscopy [14]. Note that spectroscopic techniques measure molecular concentrations, while (1) defines the delta value in atomic concentrations. Fortunately, it is easily shown that, for all practical purposes, the corresponding delta-value is identical to the result of (1) [8].

Recently, we have proposed the spectral window around 2 μm as a good compromise between the regions mentioned above, principally for two reasons [15]. First, the 2-μm region exhibits relatively strong $^{13}CO_2$ and $^{12}CO_2$ absorption features (only a factor 100 weaker than in the 4.3 μm region), among which several pairs of ro-vibrational transitions show good properties for isotope ratio measurements in terms of spectral overlap, absorption intensity and its temperature dependence [15]. Moreover, high quality, distributed feed-back (DFB) diode lasers are commercially available in this region. Implementing wavelength modulation spectroscopy to sensitively monitor the laser absorption in a multiple reflection cell, we have demonstrated the feasibility of high precision $\delta^{13}C$ determinations in mixtures of CO_2 and N_2, and provided a clear indication of the most promising way to satisfy the new demand for portable isotopic analysers [16]. A radically different approach to build a compact instrument would involve the use of a room-temperature or thermo-electrically cooled quantum cascade (QC) spectrometer at 4.3 μm, as recently discussed by Weidmann et al. [17]. However, the fabrication technology of Peltier-cooled QC lasers is not yet ready to provide high quality and reliable sources at relatively short wavelengths.

The experimental work described in the present paper is the continuation of our previously published work [16]. We have developed a simplified version of the earlier spectrometer, implementing a compact design suitable for field applications and, particularly, for in-situ isotope ratio determinations in volcanic CO_2. Most importantly, we have investigated the achievable precision and accuracy levels in real $\delta^{13}C$ determinations, which have been carried out on pure carbon dioxide samples with a known isotopic make-up. These samples have been properly selected to provide laboratory standards in a relatively wide range of $\delta^{13}C$ values, all calibrated with respect to the PDB standard by means of IRMS. We have carefully considered the main factors influencing the spectroscopic determination of an isotope ratio, such as the detection sensitivity, the detector's responsivity, the pressure and temperature dependencies of the selected line pair. Moreover, we report on a detailed investigation of the systematic deviations that may arise from a different chemical composition of sample and reference gases. Addressing this issue is of great importance for field applications of our spectrometer and, in particular, for isotope analysis in volcanic gases [18].

2 Experimental section

The experimental set-up, mounted on a 60×60 cm^2 breadboard, is depicted in Fig. 1. It is based on a room-temperature distributed feed-back (DFB) diode laser emitting a single mode at 2.008 micron (furnished by the German company Nanoplus, Nanosystems and Technologies, GmbH) with an output power of 3 mW. The diode laser is driven by a control unit (ILX-Lightwave, model LDC-3722B), capable of providing both the injection current and the temperature stabilization. The laser beam is first collimated by an AR-coated aspheric lens and then split by a 50% beam splitter. Of the resulting two beams, one makes a single pass through a 35-cm long absorption cell filled with a CO_2 gas sample, while the other traverses an identical cell filled with a reference gas (the working standard). The gas pressure inside the approximately 100 cm^3-volume cells is measured by a pair of 100-Torr capacitance gauges (Varian, mod. VCMT12TDA) with an accu-

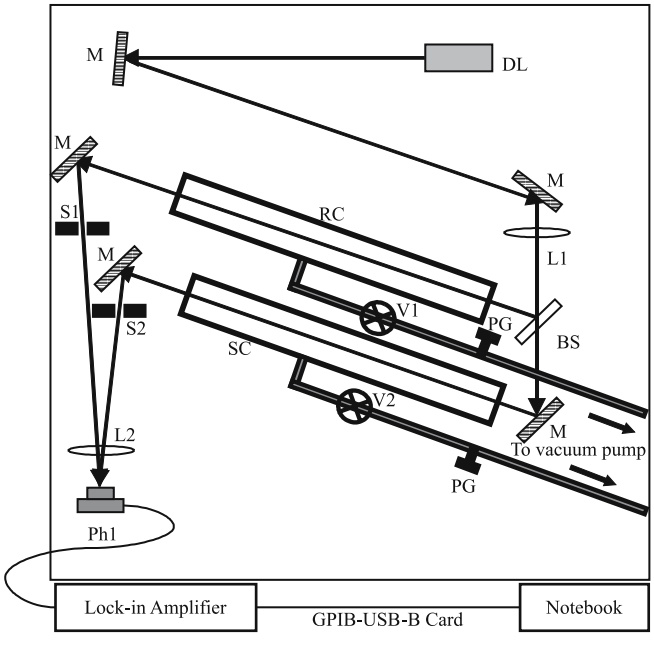

FIGURE 1 Sketch of the diode laser spectrometer. Abbreviations are as follow: DL, diode laser; M, mirror; BS, 50% beam splitter; L1 and L2, lenses with focal lengths of 1-m and 5-cm, respectively; PG, pressure gauge; V, pneumatically powered valve; S, electronic shutter; Ph, photodiode; RC and SC, reference and sample cells

racy of 0.25% and maintained at a value of 13.5 Torr. The maximum pressure difference between the two cells can be as small as 0.0675 Torr and, consequently, does not influence the measured δ-value. Each cell is equipped with two AR-coated and wedged optical windows. The transmitted beams are monitored by a single pre-amplified, thermoelectrically cooled, extended InGaAs photodiode, with an active area of 1 mm^2. A pair of electronic shutters enables the alternate blocking of one of the two beams, activating only one beam at a time. Each shutter (Newport, model 845HP-02) basically consists in a single moving blade, whose driving electric signals are generated according to the diagram reported in Fig. 2. Absorption of laser radiation is sensitively monitored using wavelength modulation spectroscopy (WMS) with 1st harmonic detection, at a modulation index of 2. For this purpose, the laser frequency is modulated at 7.45 kHz by adding a sinusoidal signal to the injection current, and a digital lock-in amplifier (Perkin Elmer, model 7265) is employed for phase-sensitive detection of the modulated absorption signals registered by the photodiode. Hence, both transmissions are monitored by the same detector and processed by the same lock-in amplifier. This sequential approach represents the main novelty with respect to our previous work, in which a simultaneous, two-detector scheme was implemented, and offers the advantage of avoiding possible systematic deviations arising from the otherwise simultaneous use of two independent detection channels. Indeed, when using two photodiodes, a small but different non-linear component of the responsitivity may influence the spectroscopic determination of the isotope ratio if a variation of the laser power takes place during a laser frequency scan, as happens in our case. Another approach would have been to use a single gas cell, and to carry out the sample and reference measurements sequentially, such as done, for example, by McManus and co-workers [10]. However, in this case extreme care has to be taken to insure that the optical and temperature stability of the apparatus is maintained over periods longer than one sample and reference measurement cycle. Moreover, the reference gas consumption would increase dramatically.

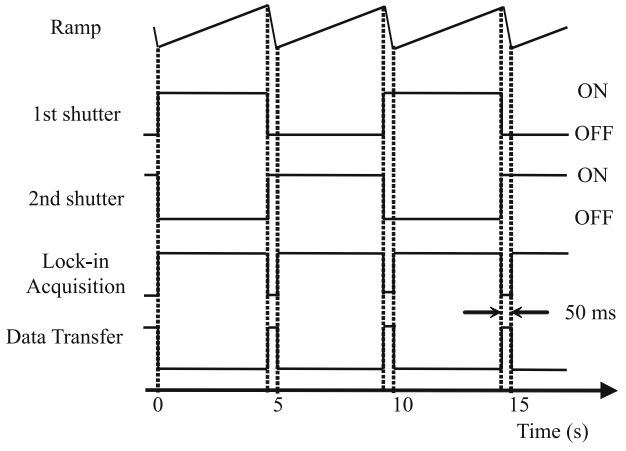

FIGURE 2 Timing diagram of the spectrometer operation. The shutters enable the alternate registration of the sample and reference spectra. Each spectrum, acquired during the slow rise of the ramp signal, is stored in the buffer of the digital lock-in amplifier and transferred to the laptop computer during the rapid falling slope

The laser frequency is periodically scanned between 4977.5 cm^{-1} and 4978.5 cm^{-1} by means of an asymmetric triangular wave at 0.2 Hz. Spectra acquisition is carried out according to the timing diagram shown in Fig. 2. A full acquisition cycle requires two consecutive slow rising ramps to recover a pair of sample and reference spectra. During this time interval, the digital lock-in amplifier operates synchronously with the ramp generator (see the 1st and 4th traces, from the top, in Fig. 2). A laptop computer, executing a LABVIEW® program and interfaced to the experiment through a GPIB-USB-B board, controls the lock-in amplifier setting, as well as the shutter apertures, and performs the spectra acquisition. Particularly, at the end of each single ramp, the computer generates a pair of voltage signals to switch the two shutters, as illustrated in the 2nd and 3rd traces of Fig. 2. The overall system allows for a continuous operation in a fully automated way for several hours. The spectra are initially stored in the buffer of the digital lock-in amplifier as data vectors of 1k-record length and a 16-bit vertical resolution, and subsequently transferred to the computer. The lock-in time constant is 20 ms with a 24-dB/octave digital filter, leading to an equivalent noise bandwidth of 6 Hz. The influence of the lock-in integration time on the absorption spectra, when the beams are alternatively blocked, can be neglected if the laser frequency scan is sufficiently wide and slow, as it was in our case. Signal averaging over several scans (between 10 and 50) is performed to further reduce the detection bandwidth, with the aim of increasing the signal-to-noise ratio of the recorded spectra.

Apart from the turbo-molecular pump (Pfeiffer Vacuum, model DCU), the gas handling system of the sample and reference gas cells is independent, in order to avoid any cross-contamination. Electro-pneumatic valves enable computer control of gas admission to the static cells, as well as their evacuation between the different sample measurements.

The breadboard is covered by a thermally insulating box with four ventilators inside, in order to facilitate thermal exchanges between all the components. This system was found to be very efficient in ensuring a uniform temperature inside the box. Particularly, differential temperatures between the two cells could not be detected within the uncertainty (0.1 K) of our thermocouples.

For the purposes of the present work, we used four different carbon dioxide samples with a known isotopic composition, referred to the PDB standard. Two of them, R_1 and R_2, respectively with δ^{13}C values of -39.0 ± 0.2‰ and -25.4 ± 0.2‰, were furnished by the Messer Griesheim company. These two were both used at different times as the machine reference gas (i.e., the working standard). The remaining two

Sample	Reference	LS values (‰)	IRMS values (‰)
S_2	R_1	-27.4 ± 0.2	-27.68 ± 0.02
R_1	R_1	0.08 ± 0.13	0.00 ± 0.02
S_1	R_2	7.87 ± 0.16	7.18 ± 0.02
R_2	R_1	13.9 ± 0.2	14.15 ± 0.02
S_1	R_1	22.2 ± 0.3	21.40 ± 0.02

TABLE 1 Isotope ratio determinations by means of laser spectrometry (LS values) and IRMS

samples, S_1 and S_2, were calibrated by means of a dual-inlet IRMS machine (Thermoquest, model Delta-Plus), using R_1 as the reference gas. They exhibited δ^{13}C values of -18.4 ± 0.2‰ and -65.6 ± 0.2‰, respectively and were treated as "unknown" samples in the validation study described here. Table 1 (in the first two columns) gives an overview of the available gases and in which combinations of sample and reference they were used.

3 Results and discussion

An example of the acquired spectra is shown in Fig. 3. The two lines were assigned to the $^{13}CO_2$ $P(16)$ component of the $2\nu_1+\nu_3$ vibrational band, and to the $^{12}CO_2$ $R(17)$ line of the $2\nu_1+\nu_2^1-\nu_2^1+\nu_3$ band, according to the HITRAN database [19]. The lower levels of these transitions are 106 cm^{-1} and 787 cm^{-1}, in energy, respectively. This translates in a temperature dependent apparent shift of the δ^{13}C measurement of 11‰ per Kelvin [15]. Signal averaging over 50 scans was performed to reduce the equivalent noise bandwidth down to 0.12 Hz, with the aim of optimising the signal-to-noise ratio (S/N) and, consequently, the reproducibility in δ^{13}C determinations, as it will be explained further in this section. The combined use of the WMS technique and signal averaging enabled us to reach a S/N value of about 10 000, for the $^{12}CO_2$ $R(17)$ line, corresponding to a detection limit of 5×10^{-6}, expressed in terms of the minimum detectable fractional absorption at a S/N = 1. The main limitation to the sensitivity was ascribed to periodic background signals (fringes) arising from spurious optical interference effects, which exhibited a period much smaller than the Doppler linewidth. It is worth noting that the reference and sample arms of the spectrometer presented different interference fringes, thus limiting the achievable precision as well. Apart from the sensitivity, a further advantage of WMS with respect to direct detection of absorption is the straightforward way of achieving background flattening, which is shown in Fig. 3. Although a similar effect could be obtained also with direct detection of absorption, provided that a balanced dual-beam strategy is implemented or a procedure of background subtraction is adopted, WMS is expected to ensure a better stability of the residual background and, consequently, a better experimental reproducibility, because of the intrinsic nature of the effect.

The δ-values were retrieved through a quantitative comparison of sample and reference spectra, consisting in a line-by-line non-linear least squares fit of the sample signal to the sum of the reference signal and a quadratic baseline, as explained elsewhere [20]. The main advantage of this data analysis procedure over that in which the individual spectral features are fit to a theoretical line profile, is that no knowledge of the exact frequency scale, nor line profile, is required. Briefly, a MATLAB program first determines the baseline, the line centres, as well as the linewidths (FWHM). Subsequently, it performs for each isotopologue the fit as mentioned above, over a frequency range as wide as three times the linewidth. The goodness of this fit strongly influences the accuracy of the δ^{13}C determination. In this respect, it is extremely important that both sample and reference spectra are recovered with a negligible distortion level, in such a way that individual profiles can be perfectly overlapped, after a scaling operation on one of them. It is also for this reason that we decided to implement a scheme based on a single detector.

The analytical reproducibility was determined as the $1-\sigma$ standard deviation in repeated measurements. An example is shown in Fig. 4a, where the results of 10 repeated δ^{13}C determinations are reported, the two cells being filled with the same CO_2 sample at a pressure of 13.5 Torr. This value represents a good compromise between two opposite requirements: The CO_2 pressure should be the lowest possible, in order to minimise pressure broadening effects, for a reason that will be explained further down. At the same time, higher values would be preferred in order to increase the

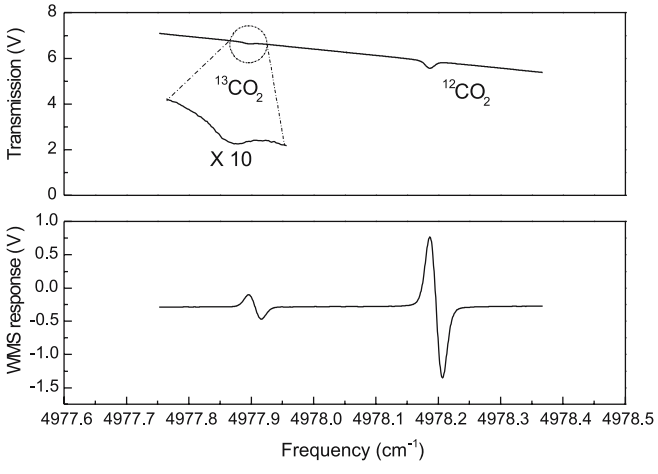

FIGURE 3 Example of an experimental absorption spectrum around 4978 cm^{-1}, at a pressure of 13.50 Torr pure CO_2. The upper trace resulted from the direct detection of absorption, while the lower one was obtained by means of wavelength modulation spectroscopy with 1st harmonic detection, using a modulation index of about 2. From the upper trace, we determined a line centre fractional absorption of 5.4%, for the $^{12}CO_2$ line and less than 1%, for the $^{13}CO_2$ line. In the latter case, we could neglect deviations from linearity of the Lambert–Beer law

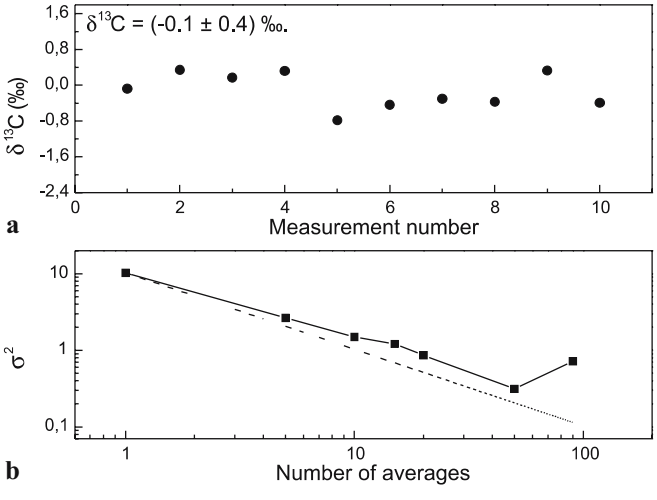

FIGURE 4 **(a)** Short-term reproducibility in the δ^{13}C determination, as resulted from 10 repeated measurements. **(b)** Variance analysis demonstrating that the optimum number of co-adds was 50. σ^2 represents the variance associated to a set of repeated measurements. The *dashed line* provides indication of the expected noise reduction for white noise

signal-to-noise ratio. Each delta-value was determined from a pair of spectra, which resulted from averaging over 50 laser scans. We found a $1-\sigma$ precision of 0.4‰ over a time span of about 80 minutes. It is worth noting that a further increase in the number of spectral co-adds did not translate into a better reproducibility. Indeed, a systematic study did not reveal any significant improvement of the precision when the number of co-adds was greater than 50. On the contrary, longer averaging times resulted in a lower precision, as mechanical and temperature drifts (causing the displacement of optical fringes) become the dominant limiting factors. This is clearly shown in Fig. 4b, where a plot of the variance, as a function of the number of spectral averages, is reported. Each variance resulted from a set of 10 δ-determinations. It is worth noting that a δ-value consistent with zero was measured, in full agreement with the fact that both cells were filled with identical CO_2 gas samples. Similar results were obtained from 27 different data sets, performed in 5 days under the same experimental conditions. Each data set consisted in 10 repeated measurements of $\delta^{13}C$, each of them resulting from an averaging procedure of sample and reference spectra over 10 laser scans. The results are shown in Fig. 5. We found an overall average value of 0.4‰, with a standard deviation of 0.7‰ representing our reproducibility in the long term, also including sample handling effects. The great majority of points are consistent with zero, within three times the standard error. We observe, besides a drift towards positive values, the occurrence of periodic fluctuations, which may be ascribed to small temperature differences between the two cells. Indeed, the temperature coefficient of our line pair indicates how these fluctuations would be consistent with a maximum temperature difference of about 0.1 K. However, high precision differential temperature measurements would be necessary in order to confirm this hypothesis. The long-term reproducibility test also demonstrated the capability of our spectrometer of operating continuously for several days.

To validate the instrument and check its calibration, we performed isotope ratio measurements on several pairs of sample and reference gases. In Table 1, the laser spectroscopic (LS) determinations are compared with the IRMS data. All the values are reported using the δ-notation, with R_1 or R_2 as standard materials, and they are not referred to the PDB standard. It is relevant to note that the uncertainty on the values of the last column is given by the accuracy of the IRMS machine. Each LS value corresponded to a set of 10 determinations, averaging the absorption spectra over 50 laser scans, the reported uncertainties being one standard error. We may note a good agreement, which is more evident from Fig. 6, where the LS against IRMS data are plotted. Here, a linear regression shows a slope equal to unity within the statistical uncertainty. Furthermore, the root-mean-square value of the residuals was found to be 0.5‰. This value gives a good indication of the overall uncertainty in LS determinations, also including possible systematic deviations. It is also consistent with the results we observed in the zero test of Fig. 5, thus confirming that systematic deviations are mostly due to temperature drifts between the two cells.

Our instrument was designed and developed for field applications in volcanic sites.

Very recently, we have demonstrated that our instrument is ideally suited to make in-situ measurements with a good temporal coverage [18]. Moreover, as the cost of the instrumentation is only a fraction of that of IRMS, it becomes possible to install multiple instruments and thus increase the spatial coverage also. Nonetheless, as already mentioned in [18], the application of our method requires the sampling of the volcanic emission followed by a CO_2 extraction, with an efficiency of 100% if we want to avoid systematic deviations in the $\delta^{13}C$ determination, considering that the reference material is a pure CO_2 sample. Indeed, the CO_2 mixing ratio in a volcanic fluid can roughly vary between 1% up to 50%, depending on the kind of volcano. Here, we have investigated this issue in quite more detail with respect to [18] and are able to show that a possible dilution of the sampled CO_2 gas is much less critical than one could expect. More precisely, we show that one can calculate the systematic error, which would be observed

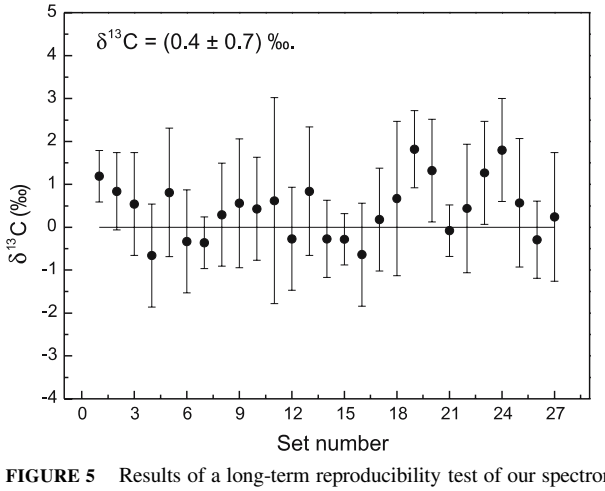

FIGURE 5 Results of a long-term reproducibility test of our spectrometer. Sample and reference cells were filled with the same CO_2 gas, at a constant pressure of 13.5 Torr. After each data set, the two cells were evacuated and refilled. Each *point* represents the mean value over ten repeated $\delta^{13}C$ determinations, which in turn are obtained from the average over ten laser scans. The error bar represents 3 times the standard error

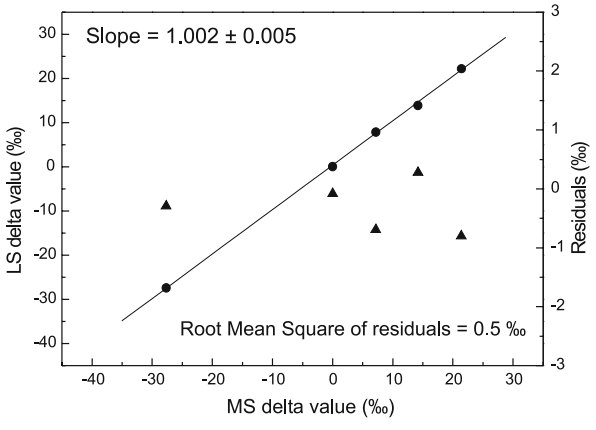

FIGURE 6 Test of the calibrated accuracy, showing the measured data (*circles*) and the linear regression line. Residuals (*triangles*), calculated as the difference between LS and MS values, are also shown. Error bars are included in the size of each point. The slope of the linear regression is consistent with unity

if a dilution of the CO_2 sample occurs, and correct the measured result accordingly, without seriously compromising the overall accuracy.

Suppose that the two gas cells are filled to exactly the same pressure, but the sampled gas has a mixing ratio lower than unity (i.e., lower than the reference gas). Then, taking into account the Lambert–Beer law, the ratio between the $^{13}CO_2$ and $^{12}CO_2$ absorptions will more closely represent the corresponding ratio of number densities in the sample cell rather than in the reference cell. Since the observed WMS signal is, to a first approximation, proportional to the line centre fractional absorption [12], the same conclusion is true for the measured $^{13}CO_2$ and $^{12}CO_2$ signals. Moreover, the $^{12}CO_2$ line absorbs more strongly than the $^{13}CO_2$ line, such that the measured $^{13}C/^{12}C$ ratio is overestimating the true number density ratio, and the more so the higher is the fractional absorption (thus at higher CO_2 concentrations in the gas cell). Consequently, the δ-value calculated from the measured WMS signals underestimates the true δ-value. We stress that this effect is entirely due to the nature of the Lambert–Beer law, in combination with the fact WMS yields a signal which is proportional to the line centre fractional absorption.

We also note that, although the sample and reference cells were filled to the same total pressure (within the accuracy of the two pressure gauges), the different chemical composition could result in different widths and shapes of the individual lines, which could potentially lead to a systematic error, as our data analysis does not truly integrate over the entire line shape. However, in our experiment, the dominant line broadening mechanism is the Doppler effect and, consequently, the line shape becomes insensitive to changes in the chemical composition and partial pressures. Indeed, the selected lines have a Doppler width that is about a factor 3 larger than the collision width, at our working temperature and pressure. Hence, a change in the homogeneous width at a level of 1% translates into a percentage variation of the width of the Voigt profile of less than 0.2%. A numerical simulation demonstrated that, changing the Voigt widths of the sample spectrum by this amount, while keeping constant the line widths in the reference spectrum, the δ-value deviated from the true value by less than 0.1‰.

We now proceed with the derivation of a theoretical formula for the systematic error described above, under the assumption of WMS signals proportional to the fractional absorptions, with identical total pressures in the two cells. We remind that the assumption above holds in the limit of thin samples [12].

The measured δ-value is given by:

$$\delta^{13}\mathrm{C}_{\mathrm{measured}} = \frac{{}^{13}\Delta_\mathrm{S}/{}^{13}\Delta_\mathrm{R}}{{}^{12}\Delta_\mathrm{S}/{}^{12}\Delta_\mathrm{R}} - 1, \tag{2}$$

where Δ is the line centre fractional absorption, the subscripts "R" and "S" refer to the reference and sample gases, while the superscripts indicate the $^{13}CO_2$ and $^{12}CO_2$ lines. We want to check whether this quantity provides the δ^{13}C value as defined by (1). Whereas the ratio at the numerator of (2) equals the ratio of the corresponding number densities ($^{13}N_\mathrm{S}/\,^{13}N_\mathrm{R}$), non-linearity of the Lambert–Beer law cannot be neglected for the ratio at the denominator. As a consequence, we may write:

$$\delta^{13}\mathrm{C}_{\mathrm{measured}} = \frac{\frac{{}^{13}N_\mathrm{S}}{{}^{13}N_\mathrm{R}}}{\frac{\left(1-\mathrm{e}^{-\sigma L\,{}^{12}N_\mathrm{S}}\right)}{\left(1-\mathrm{e}^{-\sigma L\,{}^{12}N_\mathrm{R}}\right)}} - 1, \tag{3}$$

in which σ is the line centre absorption cross section of the $^{12}CO_2$ line and L the optical pathlength. If X denotes the ratio between the $^{12}CO_2$ number density of the sample gas and that of the reference material, (3) can be rewritten in the following way:

$$\delta^{13}\mathrm{C}_{\mathrm{measured}} = \frac{\left(1-\mathrm{e}^{-\sigma L\,{}^{12}N_\mathrm{R}}\right){}^{13}N_\mathrm{S}}{{}^{13}N_\mathrm{R}\left(1-\left(\mathrm{e}^{-\sigma L\,{}^{12}N_\mathrm{R}}\right)^X\right)} - 1. \tag{4}$$

Multiplying and dividing the numerator by the same quantity X, we easily obtain the following equation:

$$\delta^{13}\mathrm{C}_{\mathrm{measured}} = \frac{\left(\delta^{13}\mathrm{C}+1\right)\left(1-\mathrm{e}^{-\sigma L\,{}^{12}N_\mathrm{R}}\right)X}{1-\left(\mathrm{e}^{-\sigma L\,{}^{12}N_\mathrm{R}}\right)^X} - 1, \tag{5}$$

where δ^{13}C is the true δ-value. Using again the Lambert–Beer law, (5) reduces to:

$$\delta^{13}\mathrm{C}_{\mathrm{measured}} = \left(\delta^{13}\mathrm{C}+1\right)\frac{{}^{12}\Delta_\mathrm{R}X}{1-\left(1-{}^{12}\Delta_\mathrm{R}\right)^X} - 1. \tag{6}$$

Hence, the systematic deviation, ε, will be given by:

$$\begin{aligned}\varepsilon &= \delta^{13}\mathrm{C}_{\mathrm{measured}} - \delta^{13}\mathrm{C} \\ &= \left(\delta^{13}\mathrm{C}+1\right)\left(\frac{{}^{12}\Delta_\mathrm{R}X}{1-\left(1-{}^{12}\Delta_\mathrm{R}\right)^X} - 1\right).\end{aligned} \tag{7}$$

This formula was already reported and used in [18], thus contributing to the good results we obtained in the field tests of the spectrometer. Obviously, ε equals to zero for $X = 1$. It is worth noting that (7) can be readily applied as the quantities X and Δ can be easily and precisely evaluated from the acquired sample and reference spectra.

We further tested in the laboratory the applicability of this simple model to the WMS technique. Using the same CO_2 gas, we filled the reference cell with pure CO_2 and the sample cell with a mixture of synthetic air and CO_2, paying attention to maintain the two cells at the same total pressure of 13.5 Torr. In this way, we could span the range of X-values from 0.45 to 1, with $^{12}\Delta_\mathrm{R} = 5.4\%$, measured from a direct absorption spectrum in the reference cell. Whereas the true δ^{13}C value must be equal to zero, we sought to explore whether the spectroscopic determinations follow (6). The experimental results are shown in Fig. 7. We found a good agreement with the model when X was decreased from 1 down to 0.6. For lower CO_2 densities, deviations from (6) become observable. This means that, at our level of absorption and provided that the $^{12}CO_2$ peak in the sample spectrum ranges between 60% and 100% of the corresponding peak in the reference spectrum, (6) is able to correctly predict the resulting systematic

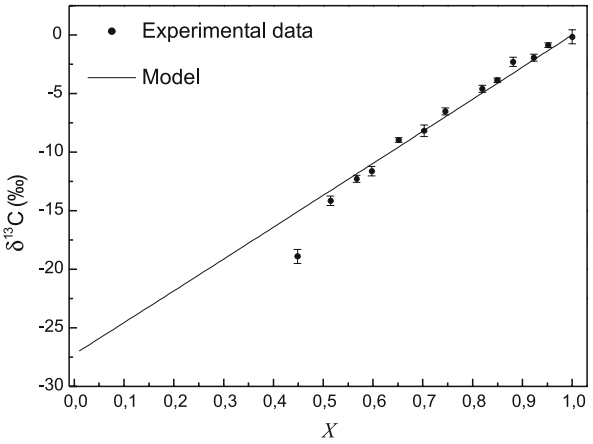

FIGURE 7 Apparent shifts in the spectroscopic determination of the $^{13}C/^{12}C$ isotope ratio in samples of synthetic air with different CO_2 concentrations. The reference material was made of CO_2 only. In each case, being the CO_2 isotopic make-up identical, the measured $\delta^{13}C$ should be equal to zero. The *line* represents the calculated systematic deviations, using the theoretical model of (6)

error within the precision of our measurements. It is noteworthy that the experimental uncertainty on X, of the order of few parts in 10^3, translates into an absolute error on the corrected δ-value of about 0.1‰, which is thus within the limits of precision of our instrument. Similarly, if the percentage absorption $^{12}\Delta_R$ had been 5.3% or 5.5% instead of 5.4%, the influence on the correction would have been smaller than 0.2‰, for X values higher than 0.6. For a larger difference of the $^{12}CO_2$ peak height between sample and reference, the non-linearity in the Lambert–Beer law starts to influence the WMS response, which will be no longer proportional to the fractional absorption and, consequently, will show a much more complicated dependence on the molecular density [12]. It is in this light that the deviation from the model of (6), clearly present in Fig. 7, can be explained.

It is relevant to mention that the non-linearity problem of the Lambert–Beer law was already taken into account by Uehara and coworkers for $^{13}C/^{12}C$ measurements in methane, implementing a radically different strategy in the determination of $\delta^{13}C$ values from WMS spectra [21]. Very briefly, they adopted a normalisation procedure of the WMS signal in order to retrieve the absorbance for each isotopologue and, hence, the isotope ratio. Nonetheless, the accuracy they could achieve with this procedure was not properly assessed, as a comparison with IRMS was reported only for a single δ-value.

4 Conclusions

We have described a laser spectroscopic method for $^{13}C/^{12}C$ isotope ratio measurements in carbon dioxide with what is arguably the simplest optical design of any such instrument reported to date. We have employed the mature and commercially easy available technology of semiconductor diode lasers at wavelengths near 2 μm, where the CO_2 molecule exhibits the strongest absorption features of the near-infrared spectral region. The simplicity of our approach has allowed to develop a reliable, compact and portable spectrometer, as well as to investigate more deeply than in previous works, the capability of laser absorption spectroscopy to provide precise and accurate $\delta^{13}C$ determinations. Calibrated accuracy was shown to be very close to the short-term precision, both being around 0.5‰. A detailed study of the systematic deviation arising from the non-linearity in the WMS response, as far as related to behaviour of the Lambert–Beer law at larger fractional absorptions (> 1%), has shown that the influence of this effect on the δ-value can be calculated, and corrected for, very precisely.

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